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Determination of flash point and cetane index in diesel using distillation curves and multivariate calibration

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HIGHLIGHTS

- ▶ PLS regression and distillation curves were effective to predict diesel flash point.
- ▶ PLS regression and distillation curves were effective to predict cetane index.
- ▶ *RMSEP* values obtained were lower than models based on spectrometric techniques.
- ▶ The models presented good accuracy and are suitable for routine analysis.

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ABSTRACT

Partial least squares regression (PLS) was used to predict flash point and cetane index of diesel using distillation curves (ASTM-D86). The low *RMSEP* values obtained, compared with other chemometric models based on spectrometric methods described in literature, and high correlation coefficients between reference and predicted values showed that PLS was efficient to determine flash point and cetane index. The model built contains diesel samples of different compositions, thus revealing the variety of fuel in the Brazilian market. Furthermore, the proposed method has two advantages: low cost and easy implementation, as it applies the results of a routine test to evaluate the quality of diesel.

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1. Introduction

Diesel is made of hydrocarbon chains, particularly saturated hydrocarbons (paraffins), unsaturated (olefins) and aromatic chains that contain from 10 to 19 carbon atoms and boil at approximately 180–370 °C [1,2]. The chemical formula is carried out by mixing several fractions from the processing stages of crude oil, and the proportions of these components adjusted in order to frame the product within legal specifications and ensure the good performance of engines.

Diesel is the most used fuel in Brazil. In 2011, approximately 52 billion liters of diesel were commercialized, including a diesel-bio-diesel mixture which represents 53% of the Brazilian market of automotive fuels [3]. This significant consumption is mainly driven by road cargo transportation, since the road network is the prime means of transport in the country.

Brazilian diesel is produced by eleven refineries distributed throughout the country. These refineries make three types of fuel for motor vehicles: S50, S500 and S1800. The commercialization of S50 diesel, with 50 mg kg⁻¹ sulfur, is available in bus fleets of some Brazilian state capitals. The commercialization of S500 diesel, with a 500 mg kg⁻¹ sulfur content, is mandatory in large urban centers, whereas S1800 diesel, with up to 1800 mg kg⁻¹ sulfur content, is available in all the other areas. At present, the three types of diesel must contain 5% biodiesel, a renewable source fuel [4] obtained by the transesterification of vegetable or animal oil, known as B5.

The quality of diesel commercialized in Brazil is assessed by means of different physico-chemical parameters in accordance with Resolution 42 of the ANP (National Agency of Petroleum, Natural Gas and Biofuels) in Fuel Quality Monitoring Program (PMQC) [5]. Diesel samples that have non-conformities in one or more physico-chemical parameters may reduce the performance of diesel engines as well as increase the consumption of fuel and the amount of pollutant gases [1].

Flash point (ASTM-D93) [6], cetane number (ASTM-D613) [7] and distillation (ASTM-D86) [8] are some of the physico-chemical

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parameters used to monitor the quality of diesel and, hence, ensure appropriate burning in the engine. Flash point is defined as the lowest temperature at which the product generates the amount of steam to ignite at controlled conditions. This characteristic is associated to flammability of fuel and shows the precautionary measures to be taken during handling, transport, storage and product use. In addition, this parameter may be used to detect contamination of fuel samples [1] with non-volatile or non-flammable materials.

The flash point test established by ASTM-D93 is carried out by exposing a diesel sample, in a closed cup, to a flame at temperature controlled warming until the steam generated burns and is detected by a quick flash [6]. A sample of diesel is suitable for use when the flash point value is above 38 °C [5]. Among the parameters evaluated in PMQC-ANP, flash point was one of the parameters responsible for higher rates of non-conformities in 2009, with 23.4%.

Cetane number is a physico-chemical parameter associated to burning of fuel in the engine. This parameter measures the ignition quality of a fuel and it directly affects both ignition and operation with load. Ignition quality is assessed by measuring the ignition delay, which is the period between injection and beginning of combustion of a fuel. Thus, a fuel with a high cetane number has a short ignition delay and starts to burn soon after it is injected in an engine [9].

The cetane number test is carried out in a mono-cylindrical engine, where fuel ignition delay is compared with the delay of a mixture of cetane and alpha-methylnaphthalene with known cetane number, in accordance with ASTM-D613 [7]. According to ANP, diesel is suitable for use when cetane number values are above 42 [5]. If the cetane number test cannot be performed, the cetane index may be used (ASTM-D4737) [10]. An equation of four variables is used to calculate this parameter, including density at 15 °C and distillation temperatures equivalent to 10%, 50% and 90% of recovered volume. For diesel, ANP determines a minimum limit of 45 [5].

In addition to standard methods, several studies have been developed in order to provide physico-chemical parameters related to flammability of diesel connecting different analytical techniques to chemometric tools, as Stepwise Multiple Linear Regression (SMLR) [11], Partial Least Squares Regression (PLS) [12–15], Principal Component Regression (PCR) [13] and Genetic Multivariate Calibration (GILS) [16].

Sikora and Salacki [11] associated near infrared spectroscopy (FT-NIR) with SMLR for the prediction of different physico-chemical properties in diesel. For cetane number, the authors found a *SEP* value (Standard Error of Prediction) of 2.48 and a correlation coefficient between actual and predicted values of 0.944, using wavelengths in the 1695 and 1915 nm interval.

Fodor et al. [12] estimated physico-chemical parameters such as flash point and cetane number in diesel samples and aviation kerosene using FT-IR (Fourier Transform Infrared Spectroscopy) associated with PLS. In some cases, as in cetane number and flash point, the models showed high *RMSEP* values (Root Mean Squared Error Prediction): 1.3 and 4.0 °C, respectively.

Soyemi et al. [13] associated near infrared spectroscopy (NIR) together with PCR and PLS chemometric tools to determine different physico-chemical parameters, including cetane number. For the latter, the *RMSEP* values obtained were 0.70 and 1.23 using PCR and PLS, respectively.

Six important physico-chemical parameters of aviation kerosene, including flash point, were determined by Andrade et al. [14] by means of a combination of FT-Raman and PLS. In the model created to predict flash point, five latent variables were able to determine more than 99% of the information, leading to the following values: *RMSEP* 1.9 °C, repeatability 2.4, and reproducibility 3.5.

Santos Jr. et al. [15] were able to establish some of the physico-chemical parameters used to evaluate the quality of diesel, including cetane number, using the neural network analysis associated with infrared technique as FTIR-ATR (Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance configuration), FTNIR and FT-Raman (Fourier Transform Raman). For the cetane number, the lowest *RMSEP* value (0.58) was obtained using the FT-Raman technique.

The determination of some parameters for the analysis of diesel, including cetane number, was carried out by Ozdemir [16] using multivariate calibration genetics associated with near infrared spectroscopy, who obtained *SEC* (Standard Error of Calibration) and *SEP* values of 1.31 and 2.11, respectively.

In order to simplify and speed-up the diesel analytical process during inspection or production procedures, this study proposes the improvement of distillation curves (an important routine test to evaluate diesel quality based on ASTM D86) to predict flash point and cetane index parameters, associated to multivariate calibration, based on PLS.

Distillation is a physico-chemical test used to measure complexity of liquid mixtures related to volatility in sample components [8]. This assay is used to verify the appropriateness of light and heavy fractions of fuel in order to have a good performance. In the case of diesel, ANP establishes maximum temperature values for 50% and 85% recovered [5].

The distillation curves created in this essay provide a data matrix whose values in percentage of recovered volume are in columns and the temperatures of each sample, in the lines, allowing the use of multivariate models. These models are an advantageous alternative to determine physico-chemical parameters because the techniques associated with multivariate calibration are quick, relatively low-priced and have proved to be useful for online inspection and control processes.

2. Experimental

2.1. Samples

For the determination of cetane index and flash point, 300 samples of diesel were collected in the east of the state of Minas Gerais and labeled with the name of the refinery of origin. Five different refineries were identified. The samples were stored in appropriate polyethylene bottles, sealed and kept at room temperature until testing.

2.2. Equipment and materials

All samples were submitted to three physico-chemical tests following the methods described in ANP's resolution [5] and the results were used for the statistical treatment. Closed-cup analyzer ISL FP93 and Herzog HDA 627 automatic distillers were used for flash point (ASTM-D93) [6], and distillation analyses (ASTM-D86) [8], respectively. For the calculation of cetane index (ASTM-D4737) specific mass values obtained from Anton Paar DMA 4500 digital densimeter (ASTM-D4052) [17] and distillation temperatures of 10%, 50% and 90% [10] were used.

2.3. Experimental procedure

2.3.1. Distillation

For the distillation procedure, 100 mL of diesel were transferred to a specific distillation flask equipped with a thermocouple sensor, and heated to keep the distillation ratio between 4 and 5 mL min⁻¹. The sample vapor was condensed and collected in a cooled test-tube (13–18 °C) and the recovered volume was measured with a

digital volume sensor. Distillation curves (distillation temperature according to the recovered volume) were obtained after correcting temperature readings to atmospheric pressure of 101.3 kPa, and volume loss after measuring residue volume, according to ASTM-D86 [8].

2.3.2. Flash point

For determining flash point, according to ASTM-D93, 70 mL of sample were transferred to a test cup equipped with a thermocouple sensor, heated and then agitated at intervals of 5–6 °C min⁻¹ and 90–120 rpm, respectively. A source of ignition was applied to the test cup at regular intervals of 1 °C starting from 23 to 28 °C below the predicted flash point. Agitation in the system was only interrupted after a distinct flash was detected. The flash point was reported as the lowest corrected temperature at barometric pressure of 101.3 kPa. In this test, the source of ignition causes combustion of sample steams and the result is expressed in °C [6].

2.3.3. Specific gravity

For this test, approximately 0.7 mL of diesel at room temperature were transferred to an oscillating sample tube, using a clean and dry syringe, and the change in oscillation frequency caused by change in the mass of the tube is used in conjunction with calibration data to determine the specific gravity of the sample [17]. After temperature stabilization of the measuring cell at 15 °C, the value of specific gravity is measured and shown in kg m⁻³.

2.3.4. Cetane index

The cetane index was calculated (CCI) using temperature values of 10%, 50% and 90% recovered (T₁₀, T₅₀ and T₉₀) and of density at 15 °C (D) in an equation of four variables [10].

$$CCI = 45.2 + 0.0892T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.420B)T_{90N} + 0.00049(T_{10N}^2 - T_{90N}^2) + 107B + 60B^2 \quad (1)$$

where $T_{10N} = T_{10} - 215$, $T_{50N} = T_{50} - 260$, $T_{90N} = T_{90} - 310$, $B = [e^{-3.5(D-0.85)}] - 1$.

2.3.5. Calibration multivariate tool

Partial least squares regression method was used to determine flash point and cetane index. This method aims at finding a small number of relevant factors that are predictive for **Y** (flash point and cetane index) and utilize **X** (distillation curves) efficiently [18]. For this purpose, Minitab Release (version 14 for Windows) and Solo (version 2007–2008 for Windows) softwares were used.

2.3.6. Evaluation of accuracy

To determine the accuracy of the proposed method, *RMSEP* (Root Mean Squared Error of Prediction) values and the residual predictive deviation (*RPD*) were calculated. *RPD* is defined as the ratio between the standard deviation of the population's reference values and the Standard Error of Prediction (*SEP*) [19]. In addition, the results of the validation set (40.5–73.4 °C flash point and 41.9–49.3 cetane index interval) obtained with the proposed method were compared with those of ASTM D93 and D4737 methods, using t test [20].

The t test was also used to compare flash point and cetane index results of ten samples from interlaboratory programs [21,22] with the proposed method. Therefore, the distillation curves of these samples were applied to the calibration set of the proposed method and the predicted values were used in t test.

2.3.7. Evaluation of repeatability and reproducibility

The evaluation of repeatability and reproducibility of the methods was carried out according to ISO-5725-2 [23]. To that end, 20 samples of diesel were used and assays for each sample were done

by three different analysts with seven replicates for each one [24], producing a total of 420 results.

3. Results and discussion

3.1. Data organization

For the construction of the matrix **X**, temperatures ranging from 4% to 91% recovered were used. Consistent with ASTM-D86 [8], the distillation of the sample must occur at a rate of 4–5 mL min⁻¹ and, to reach this rate, initial heating adjustments of the electrical resistance are necessary and may cause vigorous boiling, causing fluctuations in temperature values from the initial point of distillation up to approximately 4% recovered. Moreover, pyrolysis of larger molecules may occur in the final stage of distillation, thus reducing boiling temperature [8]. As the composition of diesel samples differs according to the origin of the oil, not every curve shows all the points in the final part of the distillation, in the 92–99% recovered. Considering these variations, the initial and final points were excluded from the data sets.

The results of the physico-chemical tests were arranged in a matrix **Y** in which the lines correspond to the samples and the columns to the results of the tests. For the prediction of these physico-chemical parameters, matrixes containing different samples in the range of 34.3–74.3 °C for flash point and 41.2–50.8 for cetane index were constructed. These matrixes were autoscaled to assign the same importance to all the variables.

In order to apply the PLS method, the samples were subdivided into training set (100 samples) and test set, or external validation (50 samples). Cross-validation “leave-one-out” [18], was used as internal validation. This method proposes the exclusion of each sample from the model and its parameter is estimated by the new model.

3.2. Flash point prediction

To predict flash point in the 34.3–74.3 °C range, the distillation curves of the training set were associated with the PLS method. To that effect, the number of latent variables to be used in the training model was chosen from the number of latent variables associated to the lower *PRESS*s (Predictive Residual Error Sum of Squares) value [25]. This was done due to the importance of selecting appropriate latent variables to obtain a good predictive model. With numerous and correlated *X*-variables there is a substantial risk of over-fitting, thus creating a well fitting model with little or no predictive power. Hence, a strict test of the predictive significance of each PLS component is necessary, stopping the test when components start to be non-significant [26]. The selection of the right amount of appropriate latent variables to be used in a model was carried out in two steps. *PRESS* values of each latent variable were compared [18] during the first step, and F test [27] was used in the second.

Fig. 1 shows that the lowest *PRESS* values are linked to latent variables in the 9–17 interval. The F test applied to these *PRESS* values indicated that the model must be constructed using nine latent variables to obtain a high predictive power model, thus avoiding over-fitting in the training set.

The *RMSEP* estimate was performed considering the external validation set, to evaluate the performance of the training model built previously, which linked multivariate calibration to distillation curves. Table 1 shows low *RMSEP* (0.69 °C) value, compared to values described in literature [12,14]. The study carried out by Fodor et al. [12] combining multivariate calibration with FT-IR presented *RMSEP* value of 4.0 °C for prediction value of flash point in middle distillate fuel samples. On the other hand, Andrade et al.

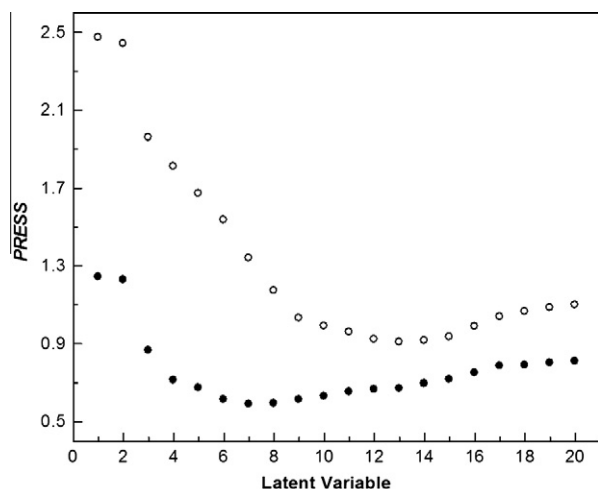


Fig. 1. PRESS values versus number of latent variables for the prediction of flash point (○) and cetane index (●).

Table 1

RMSEC, RMSEP and R values, among other parameters, obtained in the determination of flash point and cetane index using distillation curves and multivariate calibration.

Parameter	FP (°C)	CI
Number of latent variables	9	6
Correlation coefficient (R)	0.9980	0.9924
X-explained variance LV1 (%)	50.4	35.4
X-explained variance LV2 (%)	45.1	62.1
X-explained variance LV3 (%)	2.8	0.4
RMSEC	0.58	0.29
RMSEP	0.69	0.30
RPD	80.8	25.0
t Test (t_{calc}) validation set	1.87	0.45
t Test (t_{tab}) validation set	2.01	2.01
t Test (t_{calc}) interlaboratory program set	2.08	1.69
t Test (t_{tab}) interlaboratory program set	2.26	2.26
Repeatability (proposed method)	1.72	0.40
Reproducibility (proposed method)	2.40	0.45
Repeatability (standard method)	0.43	0.14
Reproducibility (standard method)	0.73	0.21
Maximum repeatability (standard method)	1.73	–
Maximum reproducibility (standard method)	4.22	–

[14] reported 1.9 °C as RMSEP value when associating FT-Raman with multivariate calibration in aviation kerosene samples. These results show the excellent performance of the training model created, even when samples of different types and origins as well as different profiles in the distillation curve were used. In a previous study [28], these slight differences in the distillation curves enabled the discrimination of diesel samples according to refinery of origin and type using chemometric techniques, as PCA (Principal Component Analysis) and LDA (Linear Discriminant Analysis). Nevertheless, the discrimination of samples according to origin and type was not an obstacle to obtain lower RMSEP values than those mentioned in literature, as well as good correlation between actual and predicted values and high RPD value.

As shown in Table 1, the RPD value to predict flash point was higher than three, which is the minimum limit determined by Zhanga et al. [29] to obtain a good prediction training model, thus indicating that the model built is highly accurate. This fact is confirmed by the high correlation (0.9980) between actual and predicted values of this training model and by the high percentage of variance explained in Y, obtained with only nine latent variables (99.6%).

In the graph of weights (Fig. 2A), the first latent variable (LV1) provided 50.4% of total variance in X, whereas the second (LV2)

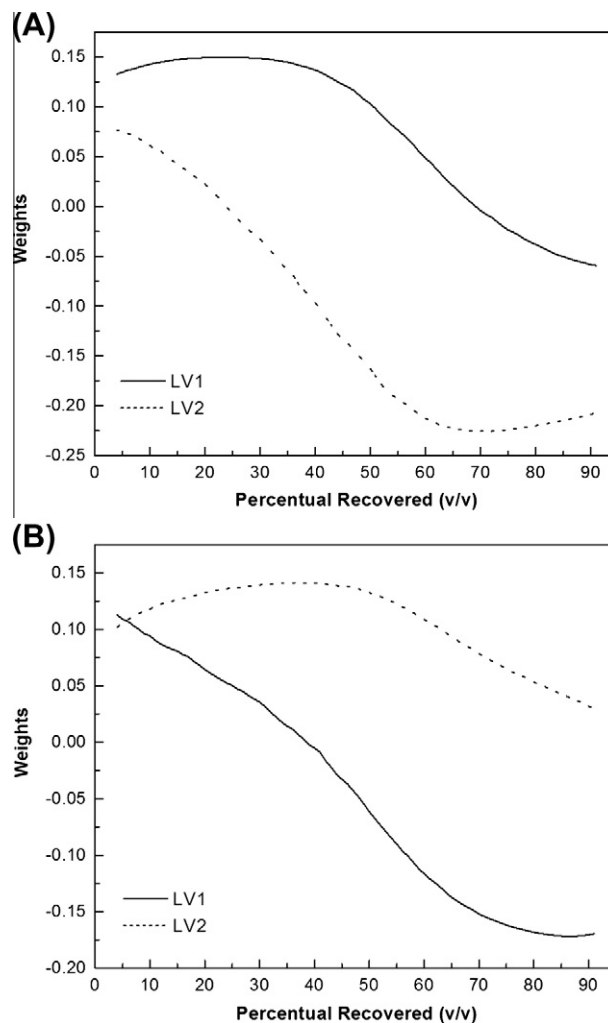


Fig. 2. Weight graphs of variables (distillation curve) for the construction of the two first latent variables (LV1 and LV2) in the determination of flash point (A) and cetane index (B).

presented 45.1%. Fig. 2A shows that the interval of 4–40% recovered in the distillation curve presented the greatest weight, with positive contribution, in the first latent variable and that the interval of 60–91% recovered is less important, with negative contribution, in the second latent variable. These observations can be explained analyzing Fig. 3A, which corresponds to average distillation curves for four intervals of the flash point.

For the most important interval of the first latent variable (beginning of distillation) it shows that flash point increases as initial temperatures rise. This is because this physico-chemical parameter is highly dependent on the content of light hydrocarbons [1], that is, the greater the quantity of light hydrocarbons, as *n*-paraffins, the lower the flash point of fuel, since these hydrocarbons are responsible for the formation of the initial steam that burns when exposed to fire. For the most important interval for the construction of the second latent variable (end of distillation) it was observed that flash point decreases as temperature increases (Fig. 3A). This distillation range of diesel has a mixture of long-chain aliphatic hydrocarbons and more complex hydrocarbons, as aromatic hydrocarbons with three rings (i.e. phenanthrene), two aromatic rings fused to a sulfur atom (dibenzothiophenes) or to a nitrogen atom (carbazoles) [30]. This mixture, unlike the mixture of hydrocarbons at the beginning of distillation, does not have an ideal behavior according to Raoult's Law [31], due to the complexity of the hydrocarbons involved. Thus,

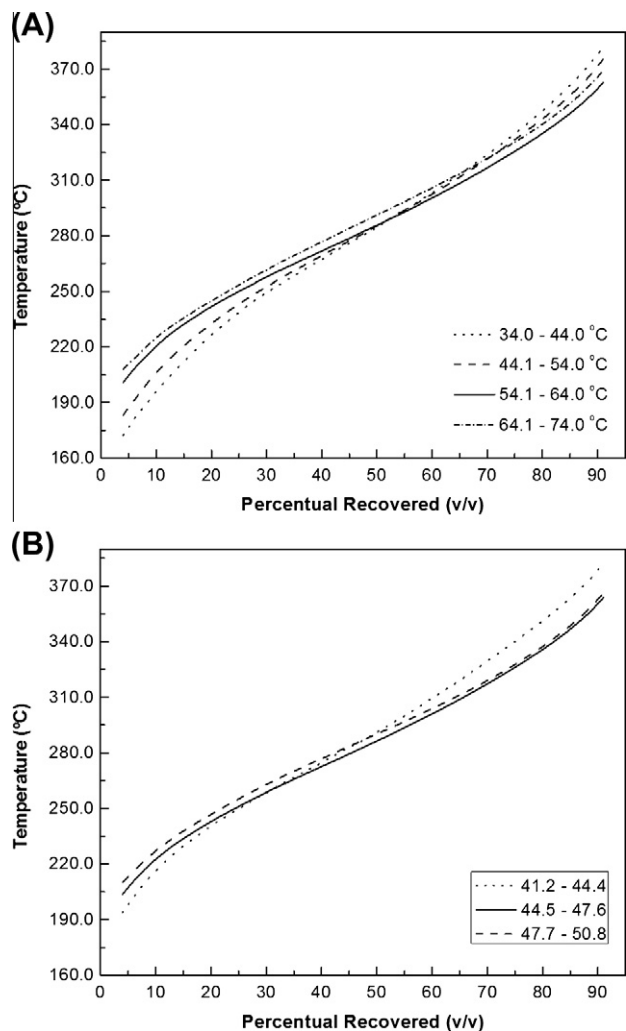


Fig. 3. Average distillation curves of samples used to determine flash point (A) and cetane index (B).

this mixture does not only depend on the vapor pressure of the individual components and the molar fraction of those components, as described in Raoult's Law [32]. It can be concluded that end of distillation, such as beginning, is also important for the prediction of diesel flash point.

In addition to *RMSEP* and *RPD* calculation, the accuracy of the proposed method was assessed comparing the results of the validation set obtained using this method with those reached with the ASTM-D93 method, using *t* test [20]. Table 1 shows that the calculated *t* value (t_{calc}) was lower than the *t* value (t_{tab}), with 95% confidence. This figure confirms there is no significant difference between the PLS model based on distillation curves and the ASTM-D93 method.

Table 1 shows that, when comparing the flash point of the interlaboratory programs samples [21,22] with the proposed method, the t_{calc} value was lower than the value of t_{tab} . Thus, it may be concluded that the proposed method was accurate and presented similar results, with 95% confidence.

The accuracy of the proposed method was assessed using the repeatability and reproducibility test [6]. Table 1 shows that repeatability and reproducibility values obtained using the proposed method are below the maximum allowed values, according to ASTM-D93 [6], indicating that the method may be used to determine flash point, although the test carried out from ASTM-D93 produced lower values. Moreover, the proposed method presented

repeatability and reproducibility values well below those obtained by Andrade et al. [14] (2.4 and 3.5, respectively) using FT-Raman and PLS.

3.3. Prediction of cetane index

In order to predict cetane index in the 41.2–50.8 range, multivariate calibration was associated to the distillation curves of samples from a different training set than that used to predict flash point. The selection of the number of latent variables was similar to the process used for the prediction of flash point (item 3.2). As shown in Fig. 1, unlike in determination of flash point, the interval with lowest *PRESS* values was from 5 to 12 latent variables. F test signaled that only six latent variables were enough to build the chemometric method.

The performance evaluation of the model was carried out with *RMSEP* calculations using external validation set. Table 1 shows that *RMSEP* value (0.30) was lower than those described by Fodor et al. (1.3) [12] and Santos Jr. et al. (0.71–0.58) [15], which reaffirms the excellent performance of the model built using distillation curves associated with PLS multivariate calibration. In a similar manner to what was observed for the determination of flash point, the different profiles in the distillation curve of the samples used, due to their varied origins and types, were not an obstacle to obtain low *RMSEP* values and high correlation between actual and predicted values, as well as high *RPD*.

The accuracy of the proposed method was demonstrated by high *RPD* values (25.0) and the correlation coefficient between actual and predicted values provided by the training model (0.9924), obtained from autoscaled data. In addition, the high percentage of variance explained in *Y* (98.5%) observed in this model, using only six latent variables, confirms the accuracy of the proposed method.

The weights graph obtained in the prediction of cetane index had a similar behavior to the weights graph in the prediction of flash point (Fig. 2). The first latent variable presented a percentage variance explained in *X* of 35.4%, whereas for the second this percentage was 62.1%.

For the first latent variable, the most relevant interval, with negative contribution, was equal to 60–91% recovered, whereas for LV2, the most significant interval, with positive contribution, was 4–40% recovered (Fig. 2B), similar to the prediction of flash point. These observations may be explained by analyzing Fig. 3B, which shows average distillation curves of three intervals of cetane index. This figure shows that when temperature corresponds to 60% of recovered volume, the cetane index decreases as temperature increases. This fact is associated to the burning of diesel, which depends on its molecular composition, as the longer the delay of engine ignition, the lower the cetane index. Thus complex hydrocarbons (i.e. aromatics) take longer to burn than light hydrocarbons (i.e. *n*-paraffins), because due to the complexity of the carbonic chain a greater branching rate is necessary than that used to burn more simple structures [9].

In a similar manner to item 3.2, the results of ASTM-D4737 and the method proposed were compared using *t* test. The value of t_{calc} obtained by the proposed method was lower than t_{tab} (Table 1), indicating that this method reaches similar results to those of the method standardized according to ASTM-D4737, with 95% confidence.

As in the prediction of flash point, the accuracy of the proposed method was also measured comparing the values obtained by this method with those of the interlaboratory programs, using *t* test. Table 1 shows that the t_{calc} value was lower than the t_{tab} value, thus indicating that the proposed method presented similar cetane index values, with 95% confidence, to those obtained by the interlaboratory programs [21,22].

The accuracy of the proposed method was evaluated using the repeatability and reproducibility calculation [10]. ASTM-D4737, which describes the cetane index calculation, does not present maximum allowed values for repeatability and reproducibility. It only states that accuracy depends on the original specific gravity and recovery temperature determinations included in the cetane index calculation [10]. Therefore, the repeatability and reproducibility values obtained by the proposed method could not be compared with the maximum allowed limits for the determination of cetane index. Table 1 shows the adequate repeatability and reproducibility values for determining cetane index, despite the test performed from ASTM-D4737 provided lower values.

4. Conclusions

Distillation curves obtained by ASTM-D86 together with PLS regression were effective to predict flash point in the 34.3–74.3 °C range and cetane index in the 41.2–50.8 range, regardless origin and type of diesel.

RMSEP values obtained in the prediction of flash point and cetane index were lower than those published in literature for models based on spectrometric techniques. This confirms the efficiency of the training models built from distillation curves, which presented good repeatability and reproducibility. Furthermore, the proposed method presented flash point and cetane index values similar to those obtained for the interlaboratory programs samples. This confirms the accuracy of the method.

The importance of fractions obtained from the distillation curve of different diesel samples in the determination of flash point and cetane index was observed in this study. Contrasting with what was expected, the study also confirmed that the heavy fractions were also significant to predict flash point.

The improvement of distillation curves associated to multivariate calibration to predict these parameters showed to be useful to accelerate the analytical process, reducing time and costs.

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